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Continuum Model of Helium Desorption Kinetics

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Helium desorption is treated in a model where the film is assumed to have the thermodynamic properties of bulk liquid and the vapor is described by kinetic theory. Equations for energy and mass conservation determine the dynamics of the system. The model resolves some puzzling features of a number of experiments, and predicts a thermally activated desorption time constant in reasonable agreement with experiment, without adjustable parameters.

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There has been intense recent interest, both experimental and theoretical, in helium desorption kinetics. New kinds of experiments, performed on submicrosecond time scales, have begun to give the subject a sound empirical basis.[1,2] There have also been important advances in microscopic theory.[3-6]

In this Letter we present a macroscopic continuum model of helium desorption. It serves the purpose of sorting out those aspects of desorption phenomena which ought to be expected from those that are genuinely surprising and in need of microscopic theoretical explanation. The model is remarkably successful in accounting for some of the apparently puzzling phenomena observed in desorption experiments, and also in relating these experiments to an earlier body of work concerned with the Kapitza resistance in adsorbed films.

Consider the situation depicted in Fig. 1. An adsorbed film of thickness δ_0 is initially in equilibrium with its vapor at temperature T_0 and pressure P_g when a heat pulse, dU/dt, suddenly enters the film from the substrate. The instantaneous temperature of the film, T_f, rises with time and its instantaneous thickness, δ_f, decreases with time until a new steady state is achieved in which desorption and readsorption from the gas are again dynamically balanced. A reference plane, chosen an appropriate distance above the substrate, separates film from gas so that the energy and mass fluxes between them can be calculated via simple kinetic theory. The gas is treated as an infinite reservoir which remains at initial conditions T_0 and P_g, unaffected by the desorption taking place, while the adsorbed film is treated as though it were a thin slice of bulk liquid in instantaneous internal thermal equilibrium, with known properties. The expression for energy balance in the film may then be written[7]

$$\frac{dU}{dt} = C_N \frac{dT_f}{dt} + (\mu_f + T_f s_l) n \frac{d\delta_f}{dt} + \alpha \left(\frac{2k_B}{\pi m}\right)^{1/2} (P_f T_f^{1/2} - P_g T_0^{1/2}), \quad (1)$$

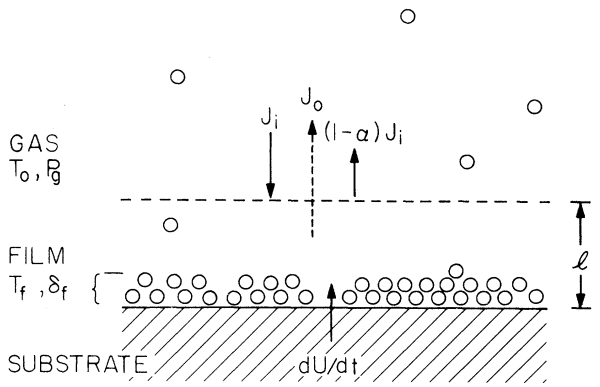

FIG. 1. The model. The adsorbed film is treated as a thin slice of bulk liquid in equilibrium at instantaneous temperature T_f and thickness δ_f. Energy flux, dU/dt, enters the film from the substrate. Mass and kinetic energy leave the film crossing a reference boundary into the gas, which remains at ambient conditions T_0 and P_g. Fluxes, J, are calculated from simple kinetic theory and detailed balance, treating the gas as ideal.

where the terms on the right represent warming of the film, latent heat of desorption, and the excess kinetic energy of warm desorbing atoms over cool adsorbing atoms, respectively. Mass conservation is given by

$$-n\frac{d\delta_f}{dt}=\frac{\alpha}{(2\pi m k_B)^{1/2}}\left(P_f T_f^{-1/2}-P_g T_0^{-1/2}\right), \quad (2)$$

Here energy and mass fluxes have been calculated using the principle of detailed balance. P_f is the pressure of a hypothetical gas that would be in instantaneous equilibrium with the film. We take it to be

$$P_f = P_0(T_f)\exp(-\gamma/\delta_f{}^3 k_B T_f), \quad (3)$$

where $-\gamma/\delta_f{}^3$ is the attractive van der Waals potential due to the substrate and P_0 is the saturated vapor pressure (SVP). We assume that the sticking coefficient, α, is given by $\alpha=1$, because that seems to be very nearly the case for bulk liquid helium.[8] The isosteric heat capacity, C_N, specific entropy of the liquid, s_l, and number density of the film, n, are taken as known functions of T_f and δ_f with the same values as those of the bulk liquid except that extensive quantities are expressed per unit area. In what amounts to the same assumption as (3), the chemical potential of the film, μ_f, is taken to equal that of the bulk liquid at the same temperature and SVP but shifted by the van der Waals potential of the substrate. The pair of coupled, nonlinear differential equations which result determine T_f and δ_f as functions of time.

These equations are easily solved in steady state, giving a film/gas temperature difference which is strictly linear in the heat input, $T_f - T_0 = R_f dU/dt$, with R_f, the thermal boundary resistance of the film/gas interface, given by[9]

$$R_f=\frac{1}{\alpha}\left(\frac{\pi m}{2k_B}\right)^{1/2}\frac{T_0^{1/2}}{P_g}. \quad (4)$$

R_f is an important parameter of the model because P_g varies over many orders of magnitude, while all other parameters vary relatively slowly.

For those experiments[1,2] in which an Ohmic heater thermally anchored to a phonon-transparent crystal serves as the substrate, it is possible to express dU/dt in terms of the electrical power delivered to the heater, the thermal impedances of the heater/crystal and heater/film interfaces, and the film temperature. It is then convenient to define the dimensionless variables

$$\chi=(\delta_f-\delta_0)/\delta_0, \quad \theta=(T_f-T_0)/T_0, \quad (5)$$

in terms of which Eqs. (1) and (2) may be linearized. For a step in the electrical power to the heater the linearized equations have solutions

$$\theta(t)=\theta_{ss}f(t), \quad \chi(t)=\chi_{ss}g(t), \quad (6)$$

with

$$f(t)=1-\theta_1\exp(-t/\tau_1)-\theta_2\exp(-t/\tau_2),$$
$$g(t)=1-\chi_1\exp(-t/\tau_1)-\chi_2\exp(-t/\tau_2). \quad (7)$$

The two decay constants turn out to differ widely in magnitude with $\tau_1 \gg \tau_2$. Furthermore, χ_2/χ_1 is of order τ_2/τ_1 so that

$$\chi \approx \chi_{ss}[1-\exp(-t/\tau_1)]. \quad (8)$$

The film thickness decays to its steady state with the single time constant τ_1. The temperature, however, displays a more complicated behavior. At pressures near SVP, $\theta_1 \approx 1$ and $\theta_2 \approx 0$.[7] The temperature then follows the film thickness, approaching its steady-state value with the same time constant τ_1. For very low pressures, however, $\theta_1 \approx 0$ and $\theta_2 \approx 1$. The temperature jumps quickly in a time $\tau_2 \ll \tau_1$ to very near its final value, remaining essentially constant while the film desorbs. This phenomenon of isothermal desorption at elevated temperature (also found when the full nonlinear equations are integrated numerically[7]) occurs because at low pressures, where R_f is large, heat is unable to escape through the film/gas interface so that initially all of dU/dt goes into raising T_f. The film then desorbs more slowly, the rate being governed by the small value of P_g which makes it difficult to transport mass to the gas. For higher pressures where R_f is smaller, desorption prevents the film from warming rapidly and so θ and χ change together.

Cole *et al.*[10] have reanalyzed the data of Ref. 1 to extract the time evolution of the temperature of a heated film. They report that thin films desorb at constant elevated temperature, just as the model predicts.

The model's predictions for the desorption time constant are shown in Fig. 2. To an excellent approximation at low pressures, τ_1 (nanoseconds) $= P_g^{-1}$ (Torr), independent of temperature. Expressing the pressure in terms of the chemical potential, μ, of the gas results in an activated form for the time constant,

$$\tau_1 = 6\times 10^{-12}\frac{\exp(-\mu/T_0)}{T_0^{2.5}} \text{ sec}. \quad (9)$$

Many theories of desorption give results of this

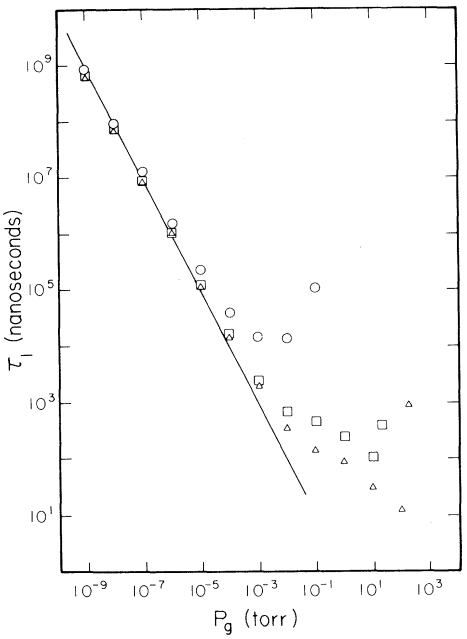

FIG. 2. Calculated τ_1 as a function of pressure for $T_0 = 1$ K (circles), 2 K (squares), and 3 K (triangles). Straight line is limiting form for τ_1 at low pressures, τ_1 (nanoseconds) = P_g^{-1} (Torr).

form, but with $-\mu$ replaced by a binding energy[11] or heat of desorption,[3] and with a wide variety of magnitudes and interpretations of the prefactor of the exponential.

Sinvani *et al.*[1] have reported desorption time constants, τ, obeying the empirical formula

$$\tau \approx 10^{-9} \exp(-2\mu_f/3k_B T_f) \text{ sec.} \quad (10)$$

We may compare this to τ_1 of the model provided we take $T_f \approx T_0$ in Eq. (10), appropriate to the linearized equations. The comparison is shown in Table I for $T_0 = 3$ K. In spite of the difference in form between Eqs. (9) and (10), there is rough agreement in magnitude, which seems significant in view of the fact that there are no adjustable parameters in the model.

The model may also be applied to phonon reflection experiments.[12-15] It has been found in these experiments that the energy reflected from an interface bearing an adsorbed helium film decreases with increasing film thickness up to about three layers, but remains unchanged thereafter.[12,14] This observation has been interpreted in terms of the behavior of the Kapitza resistance[12] or other static properties of the system,[14] but the model shows clearly that it is a consequence of desorption dynamics. If we define the reflection coefficient, F, as the fraction of energy flux returned to the crystal with He adsorbed as compared with the flux returned for a vacuum interface, the model predicts

TABLE I. Comparison of $\exp(-2\mu/3k_B T_0)$ to the time constants τ_1 predicted by the linearized model, for $T_0 = 3$ K. $\exp(-2\mu/3k_B T_0)$ is an extrapolation of the measured desorption time constants of Sinvani *et al.* (Ref. 1) expressed in nanoseconds. The experimental data do not extend to pressures above $P_g \approx 10^{-3}$ Torr.

P_g (Torr)	$\exp(-2\mu/3k_B T_0)$	τ_1 (nanoseconds)
10^{-9}	1.8×10^8	6.6×10^8
10^{-7}	8.4×10^6	8.5×10^6
10^{-5}	3.9×10^5	1.2×10^5
10^{-3}	1.8×10^4	1.9×10^3
10^{-1}	8.4×10^2	1.4×10^2
10	39	32
180	5.7	9.5×10^2

$$F(t_p) = 1 - \eta + \eta \frac{R_f}{R_f + R_K} f(t_p), \quad (11)$$

with R_f given by (4), $f(t_p)$ as in (7), where t_p is the duration of the incident phonon pulse, and with $1-\eta$ given by the value of $F(t_p)$ for the bulk liquid.[15] In the spirit of the model, R_K is the measured Kapitza resistance between the substrate and bulk liquid ^{4}He. The saturation effect is most easily analyzed for $\tau_2 \ll t_p \ll \tau_1$, a condition which is well satisfied in the experiments of Ref. 14, for example. For thin films where the gas pressure is very low, $R_f \gg R_K$. As indicated previously, $\theta_1 \approx 0$, $\theta_2 \approx 1$ in this regime so that $f(t_p) \approx 1$ and, consequently, $F(t_p) \approx 1$. The vacuum and thin-film reflection spectra are therefore very nearly the same. With increasing gas pressure, R_f becomes comparable to R_K, $\theta_1 \to 1$, $\theta_2 \to 0$ so that $f(t_p) \to t_p/\tau_1$ and therefore for films of more than a few layers and pulses short compared to τ_1, $F(t_p) \to 1-\eta$, the bulk value.

The predictions from (11) are compared in Fig. 3 with experimental data in two different temperature and pressure regimes where the important parameters of the model—R_f, θ_2, τ_1—behave quite differently. The agreement between model and experiment is excellent.

The quantitative success of the model seems surprising in view of the crudity of some of its assumptions [e.g., Eq. (3)]. The success is probably due to the fact that the phenomena of interest are principally governed by P_g, which is directly measured in experiments, rather than by quanti-

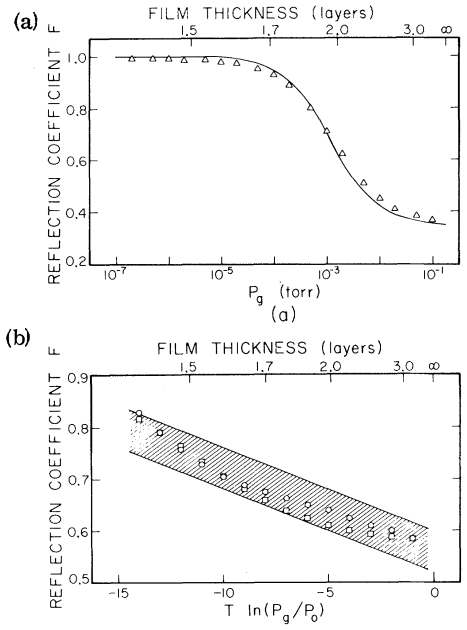

FIG. 3. (a) Predicted reflection coefficient compared with data of Dietsche and Kinder (Ref. 14) at $T = 1.04$ K. Solid line is an empirical fit to the data. Triangles represent numerical evaluation of Eq. (11) with $\eta = 0.65$ and $t_p = 100$ nsec. (b) Comparison with the data of Guo and Maris (Ref. 12). Calculated values are for $T = 1.85$ K (circles) and $T = 3.35$ K (squares) with $\eta = 0.43$ and $t_p = 100$ nsec in both cases. Cross-hatched region represents error bars cited in data.

ties such as δ_f or C_N which can only be estimated.

The model assumes that the desorbing flux from a heated helium film is identical to that from a half space of ideal gas at temperature T_f. Recent experiments have shown that neither the angular distribution[2] nor the energy distribution[16] has that assumed form. In these and related experiments the microscopic nature of desorption manifests itself, and it is these experiments that require microscopic theoretical treatment. The results we have presented here show that some of the apparently puzzling phenomena observed in desorption experiments are consequences of the subtle interplay of the conservation of energy and mass, and are adequately accounted for by a macroscopic continuum model.

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